BIODELINIFICATION AS PRETREATMENT TO ACID HYDROLYSIS OF OIL PALM TRUNK (OPT): KINETIC STUDY

WAN NUR ATIQAH BINTI WAN YUSOFF

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ABSTRACT

Acid hydrolysis is important to breakdown cellulose into its constituent sugar such as glucose. Biodelignification is one example of pretreatment. Pretreatment is applied to make the cellulose accessible to hydrolysis for further conversion such as sugar. Kinetic study is important to determine kinetic parameter for production of glucose by acid hydrolysis. The main purpose of this research is to study kinetic acid hydrolysis of OPT to produce glucose. The methodology of this research can be summarized as follow. Firstly, for untreated OPT, the research is started by run acid hydrolysis to OPT. Two stage of acid hydrolysis is applied. In this method, first, OPT is submerged in 60% sulfuric acid for 30 min and respectively at 60°C. Next, OPT is applied with 30% acid hydrolysis for 60 min and respectively at 80°C. For treated OPT, biodelignification is applied to OPT and continued with acid hydrolysis as mentioned in untreated OPT. Optimum conditions for biodelignification is as follow: temperature at 25.16°C, 7.54 pH values, 2.38 mL/12 hour moisture content and 1:2 fungi to medium ratio. RK fourth order is used to solve ordinary differential equation and the kinetic parameter obtained is analyzed. K_1, K_2 and Y_{max} are the kinetic parameters in this study which means K_1 is biomass decomposition rate, K_2 is sugar release rate and Y_{max} is glucose production. After analyze data, kinetic parameters value for treated OPT are Y_{max} = 5.266 g/l, K_1 = 0.011454 min^{-1} and K_2 = 0.015036 min^{-1} whereas for untreated OPT is Y_{max} = 4.878 g/l, K_1 = 0.007774 min^{-1} and K_2= 0.012584 min^{-1}. For conclusion, results showed that acid hydrolysis with biodelignification pretreatment give better result of kinetic parameter value this is because treated OPT have higher value of K_1, K_2 and Y_{max}. High value of K_1 means high rate to degrade biomass to produce glucose whereas high value of K_2 means that the faster time needed to achieve glucose production and high value of Y_{max} shows high glucose production. For future study, quantity of glucose obtained can be maximized by using this kinetic parameters obtained.

ABSTRAK

Hidrolisis asid adalah proses yang penting untuk memecahkan selulosa kepada konstituen gula seperti glukosa. Biodelignifikasi adalah salah satu contoh prarawatan. Prarawatan digunakan untuk membolehkan selulosa diakses oleh proses hidrolisis. Kajian kinetik adalah penting untuk menentukan parameter kinetik. Tujuan utama kajian ini adalah untuk mengkaji hidrolisis asid kinetik OPT untuk menghasilkan glukosa. Metodologi kajian ini boleh dirumuskan seperti berikut, terdapat OPT yang dirawat dan OPT yang tidak dirawat. Untuk OPT yang tidak dirawat, hanya diaplikasi dengan proses hidrolisis asid. Didalam proses hidrolisis asid terdapat dua langkah. Pertama, OPT akan direndam dalam 60% asid sulfurik selama 30minit dan pada suhu 60°C. Kedua, OPT akan direndam dalam 30% hidrolisis asid selama 60minit dan pada suhu 80°C. Untuk OPT yang dirawat, OPT diaplikasi dengan proses biodelignifikasi dan seterusnya diteruskan dengan proses hidrolisis asid. Keadaan optimum untuk biodelignifikasi adalah seperti berikut: 25.16°C, pH 7.54, kandungan lembapan 2.38 mL/12 jam dan nisbah kulat per media adalah 1:2. RK peringkat keempat digunakan untuk menganalisa persamaan kajian kinetik. Parameter kinetik adalah seperti berikut: K_1, K_2 dan Y_{max}. K_1 adalah kadar penguraian biojisim, K_2 pula adalah kadar pembebasan gula dan seterusnya Y_{max} adalah pengeluaran glukosa yang maksima. Selepas data dianalisa, nilai parameter kinetik yang diperolehi untuk OPT dirawat adalah Y_{max} = 5.266 g/l, K_1 = 0.011454min^{-1} dan K_2 = 0.015036min^{-1} manakala untuk OPT tanpa rawatan adalah seperti berikut Y_{max} = 4.878 g/l, K_1= 0.007774min^{-1} dan K_2 = 0.012584min^{-1}. Kesimpulannya, hidrolisis asid dengan prarawatan biodelignifikasi memberi hasil yang lebih baik kerana parameter kinetik menunjukkan nilai yang tinggi. Nilai K_1 yang tinggi bermaksud kadar yang tinggi untuk merendahkan biojisim untuk penghasilan glukosa manakala nilai K_2 yang tinggi bermakna masa yang lebih cepat diperlukan untuk pengeluaran glukosa dan nilai Y_{max} yang tinggi menunjukkan pengeluaran glukosa yang maksima.

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LIST OF SYMBOLS

%	Percentage
ml	Milliliter
g	Gram
°C	Degree Celsius
g/l	Gram per litre
min^{-1}	Per minute
min	Minute
h	Hours
rpm	Revolutions per minute
mmol/L	Millimole per litre
w/w	Weight over weight

LIST OF ABBREVIATIONS

OPT	Oil palm trunk
P. ostreatus	*Pleurotus ostreatus*
RK	Runge kutta
H_2SO_4	Sulfuric acid
HCL	Hydrochloric acid
EFB	Empty fruit bunch
O_2	Oxygen
CO_2	Carbon dioxide
NaOH	Sodium hydroxide
H_2O_2	Hydrogen peroxide
APEX	Ammonia fiber explosion
K_1	Biomass decomposition rate
K_2	Sugar release rate
Y_{max}	Highest glucose production

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Malaysia is one of the world's top producers of oil palm product. Oil palm tree start bearing fruits after 30 months of field planting and will continue to be productive for the next 20 to 30 years, thus ensuring a consistent supply of oil. Around 30 years after planting, palm tree will be cut and palm tree trunk is one of the components of palm tree that will dispose. Thus, amount of this lignocellulosic waste has increased proportionally with increase of oil palm tree planting. To reduce the waste of this lignocellulosic biomass toward environment come the initiative to recycle this lignocellulosic waste to give a lot of advantages if this lignocellulosic waste is process. Oil palm trunk is one of hardwood that rich with cellulose and monomer sugar such as glucose. Thus, oil palm trunk is called as lignocellulosic biomass because rich with cellulose.

Lignocellulosic waste such as oil palm trunk waste contains cellulose, hemicellulose and lignin. To extract sugar from oil palm trunk (OPT) a process called acid hydrolysis is apply. This acid hydrolysis process can be observed by using kinetic study. Ordinary differential equation and excel solver is used to solve the kinetic equation. For better result, it is believe that the oil palm trunk must be treat with biodelignification method as pretreatment to acid hydrolysis to remove lignin content. Thus, acid hydrolysis can run the process of release glucose from OPT efficiently.

1.2 Problem Statements

Malaysia produce large amount of palm oil and wooden furniture. Thus, amount of lignocellulosic material waste is also high. By using OPT as raw material to extract glucose, environmental problem of increasingly amount of this lignocellulosic biomass can be reduced. Besides that, acid hydrolysis is needed to extract glucose from OPT but the acid hydrolysis process is believed focus much on degradation of lignin in OPT. Hence, amount of glucose that can be extracting is also less. To solve this problem, lignin content in the oil palm trunk must be degrade first, thus amount of lignin in the oil trunk will be less and consequently, acid hydrolysis can focus on extraction of glucose from OPT. The comparison of glucose content between treated OPT with biodelignification and untreated OPT can be done using kinetic study. Kinetic equation of acid hydrolysis of hardwood will be applied. Thus, comparison amount of glucose content can be observed.

1.3 Research Objective

The main purpose of this research is

i. To study kinetic acid hydrolysis of OPT to produce glucose.

1.4 Research Scopes

The scopes of this study are:

i. To apply a type of local white rod fungi (*pleurotus ostreatus*) called oyster mushroom for biodelignification process as pretreatment to acid hydrolysis.

ii. To compare the kinetic parameter of acid hydrolysis with pretreatment and without pretreatment by using kinetic study

iii. Kinetic study can be done by solve the equation chosen using RK fourth order and compare the value of kinetic parameters from acid hydrolysis of untreated OPT and treated OPT.

1.5 Rationale and Significant

By using this study, biodelignification as pretreatment to acid hydrolysis of OPT can be observe whether efficient enough to be apply. The efficiency of acid hydrolysis of untreated OPT and treated OPT could be determine from this kinetic study. This can be achieved by compare the kinetic parameters of treated and treated OPT which are K_1, K_2 and Y_{max}. Higher value of these three kinetic parameters are important as high value of K_1 means high rate to degrade biomass to produce glucose whereas K_2 shows that the faster time needed to achieve glucose production. Despite of that, higher value of Y_{max} is importance as high glucose production is needed for further application. Hence, for future study, quantity of glucose obtained can be maximized when kinetic parameters is successfully obtained.

CHAPTER 2

LITERATURE REVIEW

2.1 Acid Hydrolysis

Common acid used to treat lignocelluloses material are H_2SO_4 and HCL. Cellulose is the most abundant organic molecule however its susceptibility to hydrolysis is restricted due to the rigid lignin and hemicellulose protection. Hemicellulose can be readily hydrolyzed by dilute acids under moderate conditions, but much more extreme conditions are needed for cellulose hydrolysis. A pretreatment process is needed to improve its accessibility to hydrolytic enzymes (Mosier et al, 2005). The goal of pretreatment is to make the cellulose accessible to hydrolysis for further conversion such as its constituent sugars (Parveen et al, 2009). The factors affecting the hydrolysis of cellulose include porosity (accessible surface area) of the biomass materials, cellulose fiber crystalline, and content of both lignin and hemicellulose. The presence of lignin and hemicellulose makes the accessibility of cellulose enzymes and acids to cellulose more difficult, thus reducing the efficiency of the hydrolysis process. Pretreatment is required to alter the size and structure of the biomass, as well as its chemical composition, so that the hydrolysis of the carbohydrate fraction to monomer sugars can be achieved rapidly and with greater yields.

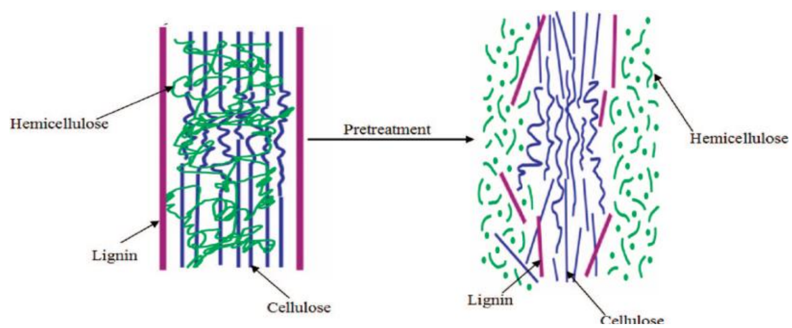

Figure 2.1 Schematic of the role of pretreatment

Ghasem et al (2007), studied single stage of acid hydrolysis process of palm oil empty fruit bunch (EFB) for production of fermentable sugar. This research was carried out under moderate temperature which is 45°C and at ambient pressure. The uses of high acid concentration for acid hydrolysis improved the reaction rate and sugar yield. Therefore, the sugar yield was found to be dependent on acid concentration and the employed temperature as well. The result shows that, for a reaction time of 40 minutes, 5 % EFB solid with 15, 20, 25 and

30 percent of HCl, EFB lignocelluloses fibers conversion of 36, 60, 65 and 80 % were achieved, respectively.

Azmalisa et al (2010), studied enzymatic hydrolysis process of the oil palm trunk fibers which can be converted into reducing sugars and subsequently be fermented to ethanol by suitable microorganisms. In this study, the conversion of cellulose to glucose with the help of cellulose enzyme accellerase TM 1000 was carried out. The results from Azmalisa et al study show that optimum conditions derived via RSM were: reaction time 13.5 h, temperature 40.8 °C, agitation rate of 167 rpm and amount of enzyme 0.4 ml. The experimental yield of glucose found to be 12.60 mmol/L under optimum condition, which compared well to the maximum predicted value, 15.15 mmol/L based on 0.5 g of substrate.

Ng et al (2011) aimed to determine total extractable starch and sugar content from OPT by using steeping method and dilute acid hydrolysis. Xylose yield the highest production using steeping method while for sugar yield, hydrolysis efficiency of 82% was obtained for conversion of OPT to glucose using two stage concentrated sulfuric acid hydrolysis. Ng et al 2011 have come to conclusion that OPT can be considered as resource of substantial amount of starch and sugar.

Anil et al (2011), studied on dilute acid pretreatment of oil seed rape straw for bioethanol production. The objective was to investigate the effect of biomass loading, acid concentration and pretreatment time on yield of sugar obtained after acid hydrolysis. The result of highest concentration of glucose is at 90 min pretreated time with glucan conversion efficiency of 81% whereas for highest concentration of sugar concentration was achieved at pretreatment of 60 min.

Chin et al (2011), studied production of glucose from oil palm trunk and sawdust of rubber wood and mixed hardwood by acid hydrolysis. This research served to identify the optimum two stage concentrated acid hydrolysis condition that can convert these three lignocellulosic biomass to glucose efficiently. Two stages concentrated sulfuric acid hydrolysis process using different acid concentration and reaction time were performed on those lignocellulosic biomass samples. The optimum results for oil palm trunk, rubber wood and mixed hardwood sawdust were obtained by using 60% acid concentration reacted for 30 min during first stage hydrolysis and subsequently followed by another 60 min reaction time with 30% acid concentration during the second stage hydrolysis. The results showed that oil palm trunk has a higher glucose conversion yield than those of rubber wood sawdust and mixed hardwood sawdust.

2.2 Raw Materials

2.2.1 Sago

Tapioca Sago is generally known as sago. Its Botanical name is "Manihot Esculenta Crantz Syn. Utilissima". This is a well known crop that is recognized by several names in the various regions where it is consumed. It is known as tapioca in India and Malaysia (FAO, 1998). Tapioca Root is the basic raw material for Sago and starch. There are about 30% to 35% starch contents generally in Indian tapioca root. Tapioca root has a high resistance to plant disease and high tolerance to extreme stress conditions such as periods of drought and poor soils. Fresh roots contain about 60 - 70% moisture, 7 - 12% protein, 5 - 13% starch (32 - 35% total carbohydrate) and trace amounts of fat (Lancaster et al., 1982; Jackson, 1990; FAO, 1998). The high starch and moisture content render it extremely perishable (Hahn 1989; Mlingi et al., 1996). Eventually, sago plant cannot be raw material in this study because will compete with food supply.

2.2.2 Rubber wood

Malaysian rubber industry has evolved through the years and transformed itself into a more integrated industry. About 80% of total wood furniture exported from Malaysia comes from rubber wood. Wood output can be obtained from planting rubber forest plantation based on 15 years cycle. Wood from tree has been traditionally regarded as waste. Total export value of rubber wood product has given by 39.44% in 2009 compared to 2000. Rubber wood is referred as an environmental friendly material with low price but its sustainable supply becoming a major concern nowadays (Ratnasingam, 2011). Despite of that, the glucose yield is lower that OPT (Chin, 2011).

2.2.3 Palm Tree

According to Alfreed (2007), palm tree is endogenous or in growing plants belonging to the same great division of vegetable kingdom as grass, bamboos, lilies and pineapple. Palm tree are almost exclusively tropical plants and very few species being found in temperate zone. The trunks of some are almost perfectly smooth, others rough with concentric rings or clothed with a woven or hairy fibrous covering, which bind together the sheathing basses of the fallen leaves.

2.2.4 Oil Palm Trunk (OPT)

OPT is a part of palm tree which will be used in this study. In this study, OPT is categorized under hardwood group. Hardwood is wood from angiosperm trees which means ovules are enclosed in an ovary and develops into the fruits after fertilizations. Hardwood is also dicotyledonous tree, compact wood, and has a more complex structure than softwood. OPT is an example of lignocellulosic material. Approximately 90% of the dry weight of most plant materials is stored in the form of cellulose, hemicellulose, lignin, and pectin (Parveen et al, 2009). The amount of waste for oil palm tree (*Elaeis guineensis*) is estimated to be around 33 million tones including empty fruit bunches, fibers and shells (IMPOB, 2009b; Mohamed and Lee, 2006). Besides that, in 2007, as much as 10, 827 tones of OPT are obtained as waste showing that these OPT are the largest contributors in waste from the agricultural industry (Goh et al., 2009). A study done by Run Chang and Tomkinson (2001) stated that the chemical composition (% dry weight, w/w) of oil palm trunk fiber is the following: cellulose 41.2%, hemicellulose 34.4%, lignin 17.1%, ash 3.4%, extractives 0.5%, and ethanol soluble 2.3%.

Table 2.1 Chemical Composition of Different Parts of the Oil Palm

Parts of oil palm	Extractives	Chemical Composition (%)		
		Holocellulose	Alpha Cellulose	Lignin
Bark	10.00	77.82	18.87	21.85
Leaves	20.60	47.7	44.53	27.35
Frond	3.50	83.13	47.76	20.15
Mid-part of trunk	14.50	72.6	50.21	20.15
Core-part of trunk	9.10	50.73	43.06	22.75
Frond	1.40	82.2	47.60	15.20
Trunk	5.35	73.06	41.02	24.51
Hardwood	0.1-7.7	71-89	31-64	14-34
Softwood	0.2-8.5	60-80	30-60	21-37

Source: Rokiah et al. (2011)

2.3 Delignification Processes as Pretreatment to Acid Hydrolysis

There are several methods delignification of hardwood but every method has their own characteristics which can be classify to advantage and disadvantage. Delignification is a process to remove the lignin from the cellulose and hemicelluloses in the lignocellulosic material. Delignification can be roughly divided into different categories: physical (milling and grinding), physicochemical (steam pretreatment/auto hydrolysis, hydrothermolysis, and wet oxidation), chemical (alkali, dilute acid, oxidizing agents, and organic solvents), biological, electrical, or a combination of these.

2.3.1 Physical Delignification

First delignification introduce is physical delignification which also call as mechanical comminution. Physical delignification is combination of chipping, grinding and milling applied to reduce cellulose crystallinity. This method is far too expensive to be used in a full scale process. Other method is Pyrolysis. In pyrolysis, cellulose rapidly decomposes to gaseous product and residual char when biomass is treated at temperature higher than 300°C. The process is enhanced when carried out in a presence of O_2. Physicochemical delignification which called steam explosion is the most commonly used for pretreatment of lignocellulosic material. Biomass is treated with high pressure saturated steam and then pressure is suddenly reduced, which makes the materials undergo explosive decomposition. Addition of sulfuric acid can improve the hydrolysis. This is one of the most cost effective delignification for hardwood.